Semiclassical theory of molecular spectral line shapes in gases*

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(Received 28 June 1973)

A semiclassical theory of the width and shift of molecular spectral lines is developed for gases. Overlapping and nonoverlapping lines are considered, within the framework of the impact approximation. Use is made of "exact" semiclassical theory of molecular collisions, recently developed by Miller and by Marcus, and of developments in the quantum mechanical theory of spectral line shapes, by introducing the former into the latter. Comparison is made with a classical-like approach.

I. INTRODUCTION

There have been a number of recent developments, both in the theory of collisional line broadening[1-14] and in the "exact" semiclassical theory[15,16] of collisions. In the present paper, these two trends are blended to yield a semiclassical theory of spectral line broadening, valid within the impact approximation and specifically for the case of foreign gas broadening for overlapping and nonoverlapping lines.

The advances in the theory of line broadening based on the "impact approximation" (an approximation which allows the collisions of perturbers with the absorbing molecule to be treated as well separated in time), include the pioneering work of Anderson,[1] who employed a classical path approximation (classical plus only zeroth order treatment of the relative motion between perturber and absorber) and a perturbative approximation for the S-matrices appearing in the line shape expression. This classical path result was later extended to overlapping lines by Baranger[2] and Kolb and Griem,[3] and by Gersten and Foley,[4] who also made detailed calculations for actual systems. Rabitz, Gordon, and Nielson[5,6] made further developments in these calculations. An all-quantum-mechanical formal treatment was developed by Baranger[7] to replace the classical path approximation and the use of perturbative expansions of the S-matrices. This formalism was made more compact with the introduction of Liouville space ("line space") formalism by Fano.[8] The latter was further developed by Ben-Reuven,[9] who introduced a practical treatment for the high-orbital–rotational degeneracy present and proceeded to treat several specific overlapping line systems.

No *ab initio* calculations for this "exact" (within the impact approximation) formalism appear to have been published. However, there have been many *ab initio calculations* using the classical path, mostly with[10] but some without[6] perturbative schemes for the internal motions. A nonperturbative classical-like model has been described by Gordon[11] and has been used recently by Gordon and co-workers[6,12] to calculate various line shapes for overlapping and nonoverlapping systems. Recent related reviews of relaxation phenomena relevant to line broadening have been given by Gordon, Klemperer, and Steinfeld[13] and by Beenakker, Knaap, and Sanctuary.[14]

The quantum mechanical formalism for the line shape[8,9] is first converted in Sec. II into a form, which contains "collision cross sections" $\sigma_{i'f';if}$. The "exact" semiclassical expressions recently developed by one of us[15] and by Miller[16] for the S-matrices[17] are then introduced into the cross-section and a semiclassical expression for the Wigner 6-j symbols[18] is also employed. Both of these appear in the expression for the line shape which is valid within the impact approximation. This expression is developed first for a linear molecule perturbed by a foreign gas in Sec. III. The extension of these expressions to related relaxation phenomena[13] is described in Sec. IV [Eqs. (4.1) and (4.4)]. The latter phenomena will also be the subject of further papers of this series.

II. QUANTUM MECHANICAL LINE SHAPE EXPRESSION

The assumptions made in each of the all-quantum-mechanical treatments for foreign gas broadening cited earlier, and used here to obtain a tractable line shape expression valid within the impact approximation, are as follows: (i) the absorber and perturber distribution functions are essentially uncorrelated, (ii) the system is dilute enough in absorber molecules that absorber–absorber interactions are minor and may be neglected, (iii) it is at low enough pressures that the approximation of binary absorber–perturber molecular collisions may be used, and (iv) the impact approximation is valid.

The spectral line shape $I(\omega)$ for electric dipole transitions is then given for overlapping lines by[9,19]

$$I(\omega) = -(1/\pi)\,\mathrm{Im} \sum_{ii'ff'} \langle f' \| \mu \| i' \rangle$$

$$\times\langle\langle\, i'f';-1,1,0\,|\,1/[\omega-\mathbf{L}_0^a-N\{\mathbf{m}(\omega)\}]\,|$$

$$\times if;-1,1,0\,\rangle\rangle\,\rho_i\,\langle i\|\mu\|f\rangle\,, \tag{2.1}$$

where Im denotes imaginary part; i and f refer to states of the absorber (emitter) before and after the optical transition, respectively; unprimed i and f denote such absorber states before collision and primed quantities such states after collision; ρ_i is the probability of finding the absorber (emitter) in state i; the -1, 1, and 0 describe the parity (-1 for an electric dipole transition) and the relevant tensorial properties of interaction with the radiation; ω is the frequency of the absorbed (emitted) radiation and, on the right hand side of (2.1), is written as positive for emission and negative for absorption;[2] $\mathbf{L}_0^a$ is the Liouville operator for the unperturbed absorber; N is the foreign gas density (perturbers); μ is the electric dipole operator; and $\{\mathbf{m}(\omega)\}$ is the binary collision Liouville operator, averaged over all perturber states:

$$\{\mathbf{m}(\omega)\}=\sum_{\xi\xi'}\rho_\xi\,\langle\langle\,\zeta'\xi'\,|\,m(\omega)\,|\,\xi\zeta\,\rangle\rangle\,, \tag{2.2}$$

where ζ and ζ' denote the state of perturber (including the translational state of absorber–perturber relative motion) before and after collision, respectively; ρ_ζ is the probability of finding this perturber in initial state ζ. When the effects of any internal states of the perturber are neglected, as with monatomic inert gas perturbers at the usual temperatures (300 °K, for example), ζ denotes only the translational state. We set $\hbar=1$ throughout. For completeness, notation and operations[9,20] for the Liouville operator L_0^a, the reduced dipole matrix elements and the (double-bracketted) Liouville vectors in (2.1) and (2.2) are summarized in Appendix A.

The operator relationship[8] between the binary collision operator $m(\omega)$ and the transition operator of scattering theory can be converted to reduced matrix form.[9b] The details and subsequent conversion to S-matrices and collision cross sections are summarized in Appendix B. One obtains

$$\langle\langle\, i'f';-1,1,0\,|\,\{m(\omega)\}\,|\,if;-1,1,0\,\rangle\rangle$$
$$=-i\int_0^\infty v\sigma_{i'f';if}\rho_v 4\pi v^2\,dv\,, \tag{2.3}$$

where $\rho_v 4\pi v^2\,dv$ is the normalized Maxwell–Boltzmann distribution and $\sigma_{i'f';if}$ is a cross section for a collision of an absorber–perturber pair

$$\sigma_{i'f';if}=(\pi/k^2)\sum_{ll'J_iJ_f}(-)^{j_i-j_i'+l-l'}(2J_i+1)(2J_f+1)$$
$$\times\begin{Bmatrix}J_f & J_i & 1\\ j_i & j_f & l\end{Bmatrix}\begin{Bmatrix}J_f & J_i & 1\\ j_i' & j_f' & l'\end{Bmatrix}[\delta_{\mathbf{i}'\mathbf{i}}\delta_{\mathbf{f}'\mathbf{f}}-S^{J_i}_{\mathbf{i}'\mathbf{i}}S^{*J_f}_{\mathbf{f}'\mathbf{f}}]\,. \tag{2.4}$$

Here, each j denotes the absorber's rotational angular momentum quantum number; i and f denote properties of the absorber (emitter) before and after an optical transition, respectively; the i and f subscripts for σ denote $\pi_i j_i$ and $\pi_f j_f$ for pure rotational lines and $\pi_i j_i n_i$ and $\pi_f j_f n_f$ for rotational–vibrational lines ($n_i\pi_i$ and $n_f\pi_f$ are the vibrational quantum numbers and parity before and after the optical transition, respectively); unprimed and primed symbols refer to pre- and postcollision quantities; l denotes the orbital angular momentum quantum number ($l=l_i=l_f$, $l'=l_i'=l_f'$); J denotes the total angular momentum quantum number (e.g., $\mathbf{J}_i=\mathbf{j}_i+\mathbf{l}=\mathbf{j}_i'+\mathbf{l}'$); and the $\mathbf{i}$ and $\mathbf{f}$ denote $\pi_i j_i l$ and $\pi_f j_f l$, respectively for pure rotational lines, and denote $\pi_i n_i j_i l$ and $\pi_f n_f j_f l$, respectively for rotational–vibrational lines; k is $\mu v/\hbar$, i.e., μv; the distribution function ρ_v is

$$\rho_v=(\mu/2\pi k_B T)^{3/2}\exp(-\mu v^2/2k_B T)\,, \tag{2.5}$$

k_B being Boltzmann's constant, T the temperature of the system, and μ the reduced mass of the absorber–perturber pair [not to be confused with the μ in (2.1)]. The S^{Ji} and S^{Jf} matrix elements in (2.4) are evaluated at different energies, e.g., as in Eq. (B19), Appendix B. Equation (2.4) is valid within the impact approximation (cf. Ref. 7).

Knowing the matrix elements of $N\{\mathbf{m}(\omega)\}$ in (2.3), those of $\mathbf{L}_0^a$ ($=E_i^0-E_f^0$) and of $\boldsymbol{\omega}(=\omega\delta_{if})$, the matrix elements of $[\omega-\mathbf{L}_0^a-N\{\mathbf{m}(\omega)\}]^{-1}$ in (2.1) can be calculated by a suitable inversion method.

Equation (2.4) is converted to semiclassical form in Sec. III.

III. SEMICLASSICAL LINE SHAPE EXPRESSION

In this section, an expression for the line shape is developed, but the variables describing vibration are excluded for brevity. These variables pose no difficulty and are included in the final expression Eq. (3.21) for overlapping lines at the end of this section.

A semiclassical expression for the 6-j symbols, appropriate for the case of two large and one small angular momenta, is[18]

$$\begin{Bmatrix}J_f & J_i & K\\ j_i & j_f & l\end{Bmatrix}=\tfrac{1}{2}(-1)^{l+j_i+J_f+K}[(j_i+\tfrac{1}{2})(J_i+\tfrac{1}{2})]^{-1/2}d^K_{\delta\lambda}(\xi)\,, \tag{3.1}$$

where $\lambda=J_f-J_i$, $\delta=j_f-j_i$ ($\lambda,\delta=\pm1,0$), and ξ is the angle between the vectors $\mathbf{j}_i$ and $\mathbf{J}_i$,

$$\cos\xi=[(J_i+\tfrac{1}{2})^2+(j_i+\tfrac{1}{2})^2-(l+\tfrac{1}{2})^2]/2(j_i+\tfrac{1}{2})(J_i+\tfrac{1}{2})\,. \tag{3.2}$$

A similar expression applies to the other 6-j symbol.

In semiclassical theory[15,16] the states i and f are most conveniently described in terms of action-angle variables. The action corresponding

to a quantum number n is $(n+\delta)h$ where δ [not to be confused with the δ in (3.1)] is, depending on the degree of freedom, frequently $\frac{1}{2}$ or, in the case of z components of angular momenta, 0. In units of $\hbar = 1$, this action variable becomes $2\pi(n+\delta)$. The coordinate canonically conjugate to the action is the angle variable w, which varies from 0 to 1. However, w is also canonically conjugate to $2\pi n$ in the appropriate sense of satisfying the correct Poisson-bracket relation for canonically conjugate quantities.[21]

A collision of an atom and a (rigid) linear molecule can be described in the center of mass system with the aid of the initial action variables $2\pi(l+\frac{1}{2})$, $2\pi(j+\frac{1}{2})$, and $2\pi(J+\frac{1}{2})$, the initial radial momentum p_R, and their canonically conjugate coordinates, w_l, w_j, w_J, and R. The dynamics of the collision are unaffected by the one remaining action variable $2\pi M$, which is the z component of **J**, and by its canonically conjugate coordinate w_M. Several of these w's, multiplied by 2π and called q's, are shown in Fig. 1. For convenience, we have set **J** along a space-fixed z axis, and so will not exhibit the (presently unneeded) angle $2\pi w_M$. The angle $2\pi w_j$ is measured in the **J** plane (plane perpendicular to **J**) in the direction indicated from the space-fixed Y axis to the line of intersection of the **j** and **l** planes, "the line of nodes ON." The angle $2\pi w_j$ is measured in the **j**-plane from ON to the position of the dipole OD. Similarly, the angle $2\pi w_l$ is measured in the **l**-plane from ON to the position of the line of centers OC of the collision partners. The postcollision coordinates w_l', w_j', w_J', and R' are canonically conjugate to the postcollision momenta, $2\pi(l'+\frac{1}{2})$, $2\pi(j'+\frac{1}{2})$, $2\pi(J'+\frac{1}{2})$, and p_R'. The angles are the same as those in Fig. 1 when primes are placed on the symbols in that figure.

Finally, in our previous semiclassical papers[15] we used (w^0, R^0) and (w, R) to denote initial and final coordinates, respectively, and $(2\pi n, p_R^0)$ and $(2\pi\bar{n}, p_R)$ to denote their canonically conjugate variables. We have now modified the notation so that these quantities are now (w, R), (w', R'), $(2\pi n, p_R)$, and $(2\pi n', p_R')$, respectively, to conform with a common line broadening practice of using unprimed and primed variables to represent pre- and postcollision quantities.

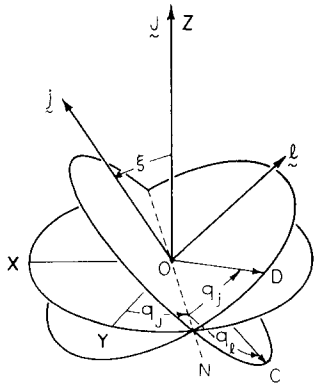

FIG. 1. Variables describing internal coordinates q_j, q_l, and q_J for the motion of an atom and rigid rotor. The rotor axis lies along OD and the line of centers of the collision partners lies along OC, at any instant of time. The q's are 2π times the corresponding w's.

The semiclassical expression for the S-matrix can be written as[22]

$$S^{J_i}_{j_i' l'; j_i l} = \sum \left| -i\partial(j_i', l')/\partial(w_{j_i}, w_l) \right|^{-1/2} \times \exp\left[iF_4(j_i' l' J_i E_i; j_i l J_i E_i) + \tfrac{1}{2}(l + l' + 1)\pi \right]. \tag{3.3}$$

F_4 is a classical mechanical generating function,[23] for transforming from the precollision momenta $j_i l J_i p_R$ to the postcollision momenta $j_i' l_i' J_i p_R'$:

$$F_4(j_i' l' J_i E; j_i l J_i E) = -\int_l^{l'} 2\pi w_l\, dl - \int_j^{j'} 2\pi w_j\, dj - \int_{p_R}^{p_R'} R\, dp_R, \tag{3.4}$$

where the integration in (3.4) is over the classical trajectory leading from the initial precollision state $j_i l J_i E$ to the desired postcollision final state $j_i' l' J_i E$. The summation in (3.3) is over all such trajectories (real or complex-valued) which lead from this initial state to this final state.

The exponent of $S^{J_i} S^{J_f *}$ in (2.4) can be written as

$$\text{exponent in } S^{J_i}_{1_i 1_i} S^{J_f *}_{1_f' 1_f'} = iF_4(j_i' l' J_i', E_i'; j_i l J_i, E_i) - iF_4^*(j_f' l' J_f' E_f'; j_f l J_f E_f). \tag{3.5}$$

Each F_4 is real valued when the relevant trajectories are real valued.

When the F_4 and F_4^* in (3.5) are expanded about a common value, retaining the first two terms of the expansion, we have

$$\begin{aligned} &F_4(j_i' l' J_i', E_i'; j_i l J_i, E_i) - F_4^*(j_f' l' J_f', E_f'; j_f l J_f, E_f) \\ &\cong 2i\Phi + \frac{\partial F_4}{\partial j_i}(j_i - j_f) + \frac{\partial F_4}{\partial j_i'}(j_i' - j_f') + \frac{\partial F_4}{\partial J_i}(J_i - J_f) \\ &\quad + \frac{\partial F_4}{\partial J_i'}(J_i' - J_f') + \frac{\partial F_4}{\partial E_i}(E_i - E_f) + \frac{\partial F_4}{\partial E_i'}(E_i' - E_f'), \end{aligned} \tag{3.6}$$

where $\Phi = \mathrm{Im} F_4$. These derivatives and Φ are evaluated at a mean value (j, j', J) of (j_i, j_i', J_i) and (j_f, j_f', J_f) and at a mean energy. We note that $J_i' = J_i$ and $J_f' = J_f$.

The partial derivatives in (3.6) are, respectively, $\bar{w}_j$, $-\bar{w}_j'$, w_J, $-w_J'$, w_E, $-w_E'$, as shown in Appendix C. Thereby, we have

$$\text{lhs of (3.6)} = 2i\Phi + \theta_1 + \theta_2, \tag{3.7}$$

where (Appendix C)

$$\theta_1 = 2\pi(\bar{w}_j'\delta' - \bar{w}_j\delta + w_J'\lambda - w_J\lambda),$$

$$\theta_2 = w_E(E_i - E_f) - w_E'(E_i' - E_f') \,, \tag{3.8}$$

$$w_E - w_E' = t' - t - (R'/v') + (R/v), \ (v<0, \ v'>0)$$

$$-\delta = j_i - j_f, \ -\delta' = j_i' - j_f', \ -\lambda = J_i - J_f, \tag{3.9}$$

and

$$\bar{w}_j = w_j - R\nu_j/v, \ \bar{w}_j' = w_j' - R'\nu_j'/v' \ . \tag{3.10}$$

$\bar{w}_j$, $\bar{w}_j'$, w_J, w_J' and $w_E' - w_E$ are constants of the trajectory, independent of the initial R and time and of the final values, R' and t'. $w_E' - w_E$ is a "collision delay time," since it is the energy derivative of the phase of an S-matrix.[24] The diagonal elements $if = i'f'$ offer no difficulty and Eqs. (3.6) and (3.7) apply. For the off-diagonal elements one actually has off-the-energy shell T-matrix elements,[7] as in Appendix C, rather than (2.4). The occurrence of these elements is also reflected in the fact that $E_i - E_f$ does not necessarily equal $E_i' - E_f'$ when $if \neq i'f'$, and hence that $E_i \neq E_i'$ or $E_f \neq E_f'$ in the T-matrix elements of line broadening. However, such differences between $E_i' - E_f'$ and $E_i - E_f$ are neglected, relative to kT, in the impact approximation.[7] Within this approximation (2.4), (3.6), and (3.7) apply to the off-diagonal elements, $if \neq i'f'$, also.

We note, too, that one pre-exponential factor of S^{J_i} in this expansion is, if we first consider the pre-exponential factor for the diagonal element $if = i'f'$, equal to the complex conjugate of that of S^{J_f}. Neglecting interference terms, we now have

$$S^{J_i}_{j_i' l' ; j_i l} S^{*J_f}_{j_f' l' ; j_f l} \cong \sum \left| \partial(j', l')/\partial(\bar{w}_j, \bar{w}_l) \right|^{-1} \times \exp\left[i(\theta_1 + \theta_2) - 2\Phi \right]. \tag{3.11}$$

The semiclassical expression for the $\sigma_{i'f';if}$ in (2.4) becomes, with the aid of (3.1) and (3.11),

$$\sigma_{i'f';if} = (\pi/k^2) \int_0^\infty (2l+1)\, dl \left(\delta_{j_i' j_i} \delta_{j_f' j_f} - \sum \int_0^\infty dl' \times \int_{|j-l|}^{j+l} dJ \frac{2J+1}{(2l+1)\sqrt{(2j+1)(2j'+1)}} \times \left| \frac{\partial(j', l')}{\partial(\bar{w}_j, \bar{w}_l)} \right|^{-1} \exp(-2\Phi + i\theta_2) D^1_{\delta'\delta}(\alpha\beta\gamma) \right), \tag{3.12}$$

where j and J denote mean values of (j_i, j_f) and (J_i, J_f), respectively, and where $D^K_{\delta'\delta}(\alpha\beta\gamma)$ is given by (3.13), with $K = 1$;

$$D^K_{\delta'\delta}(\alpha\beta\gamma) = \sum_{\lambda=-K}^{K} e^{i\theta_1} d^K_{\delta'\lambda}(\xi) d^K_{\delta'\lambda}(\xi') \ . \tag{3.13}$$

The symbol $D^K_{\delta'\delta}(\alpha\beta\gamma)$ defined by the right hand side of (3.13) proves to be the element of a rotation matrix, as shown in Appendix D, and describes the rotation of the "reduced" dipole $O\bar{D}$ into $O\bar{D}'$ via the angles α, β, and γ, as shown in Fig. 2. The angles α is the angle measured in the j-plane from the "reduced" dipole $O\bar{D}$ to the line

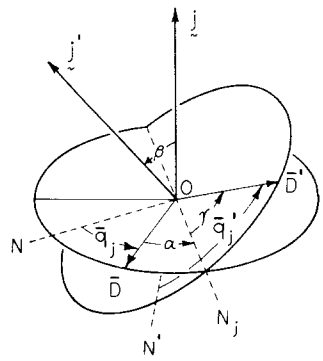

FIG. 2. Angles α, β, γ for rotating the "reduced dipole" $O\bar{D}$ into $O\bar{D}'$. The ON is the same as the ON in Fig. 1, and ON' is the corresponding quantity for the primed variables. Each $\bar{q}$ denotes $2\pi\bar{w}$, and $\bar{w} = w - R\nu/v$. ON_j is the line of intersection of the rotational plane before collision with the one after.

of nodes ON_j of the j and j' planes. The angle β is the angle of rotation about ON_j from j to j'. The angle γ is the angle measured in the j' plane from ON_j to the "reduced" dipole $O\bar{D}'$. (Thus, $\alpha\beta\gamma$ describes the rotation of $O\bar{D}$ into $O\bar{D}'$.) An angle measured from $O\bar{D}$ to the actual dipole OD in the j plane can be seen from (3.10) to be $2\pi R\nu_j/v$, while the corresponding angle from $O\bar{D}'$ to OD' in the j' plane is $2\pi R'\nu_j'/v'$. $D^K_{\delta'\delta}(\alpha\beta\gamma)$ is

$$D^K_{\delta'\delta}(\alpha\beta\gamma) = e^{i\delta'\alpha} d^K_{\delta'\delta}(\beta) e^{i\delta'\gamma} \tag{3.14}$$

following the convention in Edmonds.[25]

Inasmuch as[26]

$$\left| \partial(j', l')/\partial(\bar{w}_j, \bar{w}_l) \right|^{-1} = (\partial l'/\partial \bar{w}_l)^{-1}_{j'} (\partial j'/\partial \bar{w}_j)_{w_l} \tag{3.15}$$

we can write a term in (3.12) in the form

$$e^{-2\Phi} \left| \partial(j', l')/\partial(\bar{w}_j, \bar{w}_l) \right|^{-1} dl' = e^{-2\Phi} \left| \partial j'/\partial \bar{w}_j \right|^{-1} d\bar{w}_l = P^J_{j', ;j}(\bar{w}_l)\, d\bar{w}_l, \tag{3.16}$$

where

$$P^J_{j', ;j}(\bar{w}_l) = \left| \partial j'/\partial \bar{w}_j \right|_{\bar{w}_l} e^{-2\Phi} \ . \tag{3.17}$$

For the off-diagonal element $(if \neq i'f')$, retracing the above argument from (3.11)–(3.17) one would use in (3.19) (given later)

$$P^J_{j', ;j}(\bar{w}_l) = \left[(P^{J_i}_{j_i', ;j_i}(\bar{w}_l) P^{J_f}_{j_f', ;j_f}(\bar{w}_l) \right]^{1/2} \ . \tag{3.18}$$

$P^{J_i}_{j_i', ;j_i}(\bar{w}_l)$ is the (semiclassical) contribution to the collision probability for $j_i \to j_i'$ from the trajectory with a given j_i, l, J_i, $\bar{w}_l$, $\bar{w}_j$, and E. By specifying j_i and j_i', the value of $\bar{w}_j$ needed to reach j_i' from j_i is automatically specified, although there may be several discrete values of such a $\bar{w}_j$, for a given j_i, j_i', l, $\bar{w}_l$, and E. The summation over such discrete points is indicated by the $\sum$ in (3.12).

It is useful to introduce a further probability term:

$$\bar{P}^J_{j', ;j}(\bar{w}_l) = \{(2J+1)/(2l+1)[(2j+1)(2j'+1)]^{1/2}\} \times P^J_{j', ;j}(\bar{w}_l) \tag{3.19}$$

which gives a type of joint probability for finding a given J (there are $2J+1$ states out of a total of $(2j+1)(2l+1)\,jl$-states before collision and typically $2j'+1 \sim 2j+1$) and for reaching state j' from state j. Hence, Eq. (3.12) for rotational overlapping lines becomes

$$\sigma_{i'f',if} = (\pi/k^2)\int_0^\infty (2l+1)\,dl[\delta_{i'i}\delta_{f'f} - \sum\int_0^1 d\bar{w}_l \times \int_{|j-l|}^{j+l} dJ\,\bar{P}^J_{j'j}(\bar{w}_l)\exp(i\theta_2)\,D^1_{\delta'\delta}(\alpha\beta\gamma)] \,. \tag{3.20}$$

For the simple case of a rotating dipole, only the matrix elements of $\{m(\omega)\}$ in Eq. (2.3) for which $j_i - j_f = \pm 1$ and $j_i' - j_f' = \pm 1$ need to be calculated The method outlined there then gives the line shape for this rigid rotating dipole. (Other systems which involve additional elements, namely $j_i = j_f$ and $j_i' = j_f'$, i.e., so-called nonresonant spectra, as in the inversion of ammonia, are described by adapting the formal treatment[9b] for those cases.)

As already noted, the preceding treatment also applies to rotational–vibrational spectra of linear molecules, when the appropriate vibrational subscripts are added. The line shape prescription is thereby identical to that mentioned above except that the relaxation cross section now becomes

$$\sigma_{i'f',if} = (\pi/k^2)\int_0^\infty (2l+1)dl\,[\delta_{i'i}\delta_{f'f} - \sum\int_0^1 d\bar{w}_l \times \int_{|j-l|}^{j+l} dJ\,\bar{P}^J_{j'n';jn}(\bar{w}_l)D^J_{\delta'\delta}(\alpha\beta\gamma)\exp[i(\theta_n+\theta_2)] \,, \tag{3.21}$$

where n denotes the mean value of the vibrational quantum numbers n_i and n_f before and after the $i \to f$ optical transition; the vibrational term θ_n is given by

$$\theta_n = -2\pi\bar{w}_n'(n_i' - n_f') + 2\pi\bar{w}_n(n_i - n_f) \,, \tag{3.22}$$

where $\bar{w}_n$ is the coordinate conjugate to $2\pi n$. (If there is more than one vibration there is the appropriate sum of θ_n's.) The quantity $\bar{P}^J_{j'n';jn}(\bar{w}_l)$ becomes

$$\bar{P}^J_{j'n';jn}(\bar{w}_l) = \left|\frac{\partial(j',n')}{\partial(\bar{w}_j,\bar{w}_n)}\right|^{-1}_{\bar{w}_l} e^{-2\Phi} \times \frac{2J+1}{(2l+1)[(2j+1)(2j'+1)]^{1/2}} \,, \tag{3.23}$$

which is now the (semiclassical) contribution to the collision probability for the transitions $j \to j'$ and $n \to n'$ from trajectories having a given initial (l, J, $\bar{w}_l$; E), and, essentially, for a joint probability of having a given J. The sum $\sum$ in (3.20) is over the particular values of $\bar{w}_j$ and $\bar{w}_n$ which give the desired j' and n' for the given initial values of the remaining collisional variables. For off-diagonal elements one would use the counterpart of (3.18) instead of the first two factors in (3.23).

For the case of nonoverlapping pure rotational lines, using a rigid rotor model, the shape of a given rotational absorption line is, for states 1 and 2,

$$I(\omega) = -\frac{1}{\pi}\,|\,\langle j_1\|\,\mu\,\|j_2\rangle\,|^2 \times \mathrm{Im}\left[\frac{\rho_1}{-|\omega| - \omega_{12} + i\langle v\sigma_{12;12}\rangle} + \frac{\rho_2}{-|\omega| - \omega_{21} + i\langle v\sigma_{21;21}\rangle}\right] . \tag{3.24}$$

If 1 and 2 denote the lower and upper states, respectively, then $E_2 - E_1 > 0$; hence, we let $\omega_0 = \omega_{21} = -\omega_{12}$. We may now let ω be a positive quantity (the minus sign in $-|\omega|$ having already taken account of absorption) and let the shift and width be denoted by d and w, respectively, where $w + id = \langle v\sigma_{21;21}\rangle$. (The latter equals $\langle v\sigma_{12;12}{}^*\rangle$.) $\langle\cdots\rangle$ denotes a Maxwell–Boltzmann average over velocities. We then have

$$I(\omega) = \frac{1}{\pi}\,\mathrm{Im}\,|\,\langle j_1\|\,\mu\,\|j_2\rangle\,|^2\left[\frac{\rho_1}{\omega - \omega_0 - d - iw} + \frac{\rho_2}{\omega + \omega_0 + d - iw}\right] , \tag{3.25}$$

where $\omega > 0$ and

$$\sigma_{12;12} = (\pi/k^2)\int_0^\infty (2l+1)\,dl\,\left[1 - \sum\int_0^\infty d\bar{w}_l \times \int_{|j-l|}^{j+l} dJ\,\bar{P}^J_{j;j}(\bar{w}_l)\exp(i\theta_2)D^1_{11}(\alpha\beta\gamma)\right] . \tag{3.26}$$

The second term in (3.25) is the familiar "negative resonance" term and corresponds to the tail of an absorption centered at $-|\omega_0|$.[9b]

IV. EXTENSION TO OTHER LINE SHAPE SPECTRA

The line shape expression (2.1) can be written in a form appropriate to certain additional spectra[9a]:

$$I(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\sum_{ii'ff'}\langle f'\|X^{\Pi K}\|i'\rangle\langle\langle i'f';\ \Pi KQ\left|\frac{1}{\omega\mathbf{-L}_0^a - N\{\mathbf{m}(\omega)\}}\right|if;\ \Pi KQ\rangle\rangle\,\rho_i\langle i\|X^{\Pi K}\|f\rangle \,, \tag{4.1}$$

where the operator describing the interaction of the system with the radiation is described in general by a multipole Kth-order tensor operator $X^{\Pi K}$ (for the 2^K-pole interaction with radiation), Q indicates a particular one of $2K+1$ standard irreducible components of that operator, and Π is the parity of that operator. For the electric dipole spectra in the previous sections we had $K = 1$, $\Pi = -1$, $X^{\Pi K} = \mu$ and, for radiation polarized along a space-fixed z axis, $Q = 0$. For depolarized Raman scattering, $K = 2$. In the case of application of (4.1) to the inver-

sion spectrum of the ammonia molecule, II must be taken into account.

Instead of (2.3) we now have

$$\langle\langle i'f';\ \Pi KQ\,|\,\{m(\omega)\}\,|\,\Pi KQ\rangle\rangle = -i\int_0^\infty v\sigma_{i'f';if}\rho_v 4\pi v^2\,dv. \tag{4.2}$$

The matrix element for $\{\mathbf{m}(\omega)\}$ is diagonal in K, Q, and Π for isotropic gases and independent of Q, as shown by Ben-Reuven.[9] Its properties in the presence of applied fields have been discussed by Snider and Sanctuary.[8] In the present case of a general K, $\{\mathbf{m}(\omega)\}$ in Eq. (4.1) is again found to be given by the right hand side of (2.3), but now, as shown in Appendix B, the cross section $\sigma_{i'f';if}$ is that for a system of the given K. It is independent of Q and is denoted by $\sigma^K_{i'f';if}$:

$$\sigma^K_{i'f';if} = \frac{\pi}{k^2}\sum_{ll'J_iJ_f}(-)^{j_i-j_i'+l-l'}(2J_i+1)(2J_f+1)$$

$$\times\begin{Bmatrix} j_i' & K & j_f' \\ J_f & l' & J_i\end{Bmatrix}\begin{Bmatrix} j_i & K & j_f \\ J_f & l & J_i\end{Bmatrix}[\delta_{l'l}\delta_{f'f} - S^{J_i}_{l'i}S^{J_f*}_{f'f}], \tag{4.3}$$

where i in σ refers to the appropriate quantum numbers and $\mathbf{i}$ consists of this i, J_i, and l. This cross section may be readily expressed semiclassically for rotation–vibration spectra by noting that the only difference between (2.4) and (4.3) is the appearance of a K instead of a 1. Hence,

$$\sigma^K_{i'f';if} = (\pi/k^2)\int_0^\infty (2l+1)\,dl\,[\delta_{i'i}\delta_{f'f} - \sum\int_0^1 d\bar{w}_l\int_{|j-l|}^{j+l} dJ$$

$$\times \bar{P}^J_{j'n';jn}(\bar{w}_l)e^{i(\theta_2+\theta_n)}D^K_{\delta'\delta}(\alpha\beta\gamma)] \tag{4.4}$$

is the cross section.

V. DISCUSSION

The diagonal elements in $\sigma_{i'f';if}$ describe the shift and width of nonoverlapping spectral lines. The off-diagonal elements couple line $i\to f$ with line $i'\to f'$ and "transfer intensity" from one to the other, as well as causing collisional narrowing. The effects of such transfers have been discussed by various authors.[6,9,11,12] The quantum mechanical expression (4.3) for $\sigma^K_{i'f';if}$ is of the same form as that stated by Gordon, Klemperer, and Steinfeld.[13]

The semiclassical expression for the line shape, given by Eqs. (4.1), (4.2), and (4.4) is seen, in its "collision cross section" $\sigma^K_{i'f';if}$, to contain several factors: a partial transition probability amplitude $\bar{P}^J_{j';j}$, a rotation matrix element $D^K(\alpha\beta\gamma)$, with the angles described in Fig. 2, and an added phase term $\exp i(\theta_2+\theta_n)$.

The various quantities appearing in Eq. (4.4) can be evaluated from numerically calculated classical trajectories. It is frequently convenient to do so with the aid of Cartesian coordinates, the choice of initial conditions being made to conform with a given initial j, l, n, J, and E, as well as with some preassigned R [the relevant results in (3.8) to (3.10) are independent of R], w_j, w_l, and w_n. The procedure for transforming from Cartesian coordinates to action-angle variables is available in the standard texts.[27] In application, one selects trajectories which lead to a particular j' and n'; only several values of w_j and w_n satisfy this condition. From the final data at some preassigned R' (the results are independent of R') one calculates the various quantities, $\bar{w}_j'$, $w_J'-w_J$, etc. In this way the integrand in Eq. (4.4) can be calculated as a function of the variables appearing there, $\bar{w}_l$, l, J, for any given line pair $i\to f$, $i'\to f'$.

It is useful to evaluate the factor $D^K_{\delta'\delta}(\alpha\beta\gamma)\times\exp i(\theta_2+\theta_n)$ in the integrand of (4.4) for several cases and interpret its phase in terms of a phase shift of the mechanical motion. We consider the diagonal elements $if=i'f'$ first. The term $D^K_{\delta'\delta}$ is given in Tables I and II for diagonal and off-diagonal elements, for the cases of $K=1$ and $K=2$, respectively.

From Eq. (3.8) and Table I we have for the RR' diagonal element, where $i\to f$ is an R-branch transition and $i'\to f'$ is also an R-branch transition,

RR' element:

phase

$$[D^K_{\delta'\delta}(\alpha\beta\gamma)e^{i(\theta_2+\theta_n)}] = \alpha+\gamma + (t'-t-R'/v'+R'/v)\times\omega_{if}+\theta_n. \tag{5.1}$$

For the PP' case we have

PP' element:

phase

$$[D^K_{\delta'\delta}(\alpha\beta\gamma)e^{i(\theta_2+\theta_n)}] = -\alpha-\gamma + (t'-t-R'/v'+R/v)\times\omega_{if}+\theta_n, \tag{5.2}$$

where ω_{if} equals E_i-E_f and so differs in (5.1) and (5.2).

The right hand sides of (5.1) and (5.2) can be shown to be related to the collisionally induced phase shift in the vibrational–rotational motion, as follows. The R and P branches of the spectrum

TABLE I. Matrix elements $D^1_{\delta'\delta}(\alpha\beta\gamma)$ for electric dipole transitions.

δ' \ δ	$(j-1)-j$ (P branch)	$j-(j-1)$ (R branch)
$(j-1)-j$ (P' branch)	$\cos^2(\beta/2)\,e^{-i(\alpha+\gamma)}$	$\sin^2(\beta/2)\,e^{i(\alpha-\gamma)}$
$j-(j-1)$ (R' branch)	$\sin^2(\beta/2)\,e^{-i(\alpha-\gamma)}$	$\cos^2(\beta/2)\,e^{i(\alpha+\gamma)}$

TABLE II. Matrix elements $D^2_{\delta'\delta}(\alpha\beta\gamma)$ for depolarized Raman scattering.

δ' \ δ	$(j-2)-j$ (O branch)	$(j-1)-(j-1)$ (Q branch)	$j-(j-2)$ (S branch)
$(j-2)-j$ (O′ branch)	$\cos^4(\beta/2)\, e^{-2i(\alpha+\gamma)}$	$\sqrt{3/8}\,\sin^2\beta\, e^{-2i\gamma}$	$\sin^4(\beta/2)\, e^{2i(\alpha-\gamma)}$
$(j-1)-(j-1)$ (Q′ branch)	$\sqrt{3/8}\,\sin^2\beta\, e^{-2i\alpha}$	$\frac{1}{2}(3\cos^2\beta-1)$	$\sqrt{3/8}\,\sin^2\beta\, e^{2i\alpha}$
$[j-(j-2)]$ (S′ branch)	$\sin^4(\beta/2)\, e^{-2i(\alpha-\gamma)}$	$\sqrt{3/8}\,\sin^2\beta\, e^{2i\gamma}$	$\cos^4(\beta/2)\, e^{2i(\alpha+\gamma)}$

arise classically from terms in which some component of the mechanical motion oscillates as $\cos 2\pi w_n \cos 2\pi w_j$, and thereby as a composite of $\cos 2\pi(w_n+w_j)$ and $\cos 2\pi(w_n-w_j)$, respectively. The time dependence of $2\pi(w_n+w_j)$ and $2\pi(w_n-w_j)$ is $(\omega_n+\omega_j)t$ and $(\omega_n-\omega_j)t$, where the ω's are angular frequencies, and so give rise to the R and P branches, respectively. We consider the R branch first, and calculate the phase of the dipole OD' in Fig. 1 relative to that of OD. The rotational phase of OD' in Fig. 2 is $2\pi\overline{w}'_j$. Hence, by (3.8) the rotational phase of OD', $2\pi w'_j$, is $2\pi(\overline{w}_j + R\nu'_j/v')$. These phases are relative to that of ON in Fig. 1. The rotational phase of OD' relative to ON_j in Fig. 2 is $2\pi(\overline{w}'_j + R'\nu'_j/v') - a'$, where a' is the angle from ON' to ON_j. Thus, introducing the angle γ defined in Fig. 2, we have

$$\text{phase } OD' (\text{relative to } ON_j) = \gamma + 2\pi R'\nu'_j/v' \quad (R' \text{ branch}). \quad (5.3)$$

A similar argument regarding OD yields

$$\text{phase } OD (\text{relative to } ON_j) = -\alpha + 2\pi R\nu_j/v \quad (R \text{ branch}). \quad (5.4)$$

The rotational phase shift η_r from OD to OD' is obtained by subtracting (5.4) from (5.3) and then subtracting the time-evolution term $\omega_j(t'-t)$ for the free rotational motion. Noting that ω_j equals $2\pi\nu_j$ and $2\pi\nu'_j (2\pi\nu'_j \cong 2\pi\nu_j)$, η_r is seen to be given by (5.5).

$$\eta_r = \alpha + \gamma + (t' - t - R'/v' + R/v)\omega_j \quad (RR' \text{ element}). \quad (5.5)$$

The vibrational phase shift η_v is, by a similar argument, equal to $2\pi(w'_n - w_n) - \omega_n(t'-t)$. Thus, using (3.10), with j's replaced by n's, we have

$$\eta_v = 2\pi(\overline{w}'_n - \overline{w}_n) - (t' - t - R'/v' + R/v)\omega_n . \quad (5.6)$$

The sum of η_r and η_v is seen to agree with the right hand side of (5.1) since ω_{if} equals $-(\omega_j+\omega_n)$ for an R branch and since θ_n is given by (3.22).

We consider next the PP' element. Here, the system behaves mechanically as though it had an angular frequency of $\omega_n - \omega_j$. The vibrational phase shift is given above by (5.6). The rotational phase shift is different, however. The phase of OD' relative to ON' is now $-2\pi(\overline{w}_j + R\nu'_j/v')$. Relative to ON_j, it is seen with the aid of Fig. 2 to be

$$\text{phase } OD' (\text{relative to } ON_j) = -\gamma - 2\pi R'\nu'_j/v' \quad (P' \text{ branch}). \quad (5.7)$$

Similarly,

$$\text{phase } OD (\text{relative to } ON_j) = \alpha - 2\pi R\nu_j/v \quad (P \text{ branch}). \quad (5.8)$$

Subtraction of (5.8) from (5.7) and *addition* of the time-evolution term $\omega_j(t'-t)$ now yields,

$$\eta_r = -\alpha - \gamma + (t' - t - R'/v' + R/v)\omega_j \quad (PP' \text{ element}), \quad (5.9)$$

where we have again set $\nu'_j \approx \nu_j = \omega_j/2\pi$.

The sum of (5.6) and (5.9) agrees with the right hand side of (5.2), which is thus, like (5.1), the rotational–vibrational phase shift.

We consider next the off-diagonal element PR', with $n_i = n'_i$ and $n_f = n'_f$ (i.e., a vibrationally diagonal element). From Table II we have

PR' element:

$$\text{phase } [D^K_{\delta'\delta}(\alpha\beta\gamma) e^{i(\theta_2+\theta_n)}] = -\alpha + \gamma + \theta_2 + \theta_n . \quad (5.10)$$

However, differences in $E_i - E_f$ and $E'_i - E'_f$ are ignored within the impact approximation.[7] If we replace them by $\frac{1}{2}(\omega_{if} + \omega_{i'f'})$, (3.8) yields

$$\theta_2 \approx \tfrac{1}{2}(w_E - w_{E'})(\omega_{if} + \omega_{i'f'}) . \quad (5.11)$$

One then finds,

$$\text{phase } [D^K_{\delta'\delta}(\alpha\beta\gamma) e^{i(\theta_2+\theta_n)}] \cong -\alpha + \gamma + \eta_v , \quad (5.12)$$

where η_v is given by (5.6). One might expect $\alpha \cong \gamma$.

To compare (5.12) with the estimated phase shift arising from rotational–vibrational motion we shall need to introduce a "midpoint" of the collision and shall let it occur at $t=0$. The collision time t_c can introduce an uncertainty in locating this "midpoint" but uncertainties of the order of t_c are neglected by the impact approximation.[7] The phase of the dipole OD' relative to ON_j is again given by (5.3), and one subtracts $\omega_j t'$ to calculate the rotational phase shift contribution from the midpoint of the collision to the end, i.e., from $t=0$ to t'. Thus, this contribution to η_r is $\gamma + 2\pi R'\nu'_j/v' - \omega'_j t'$. The phase of OD at the initial time t ($t<0$) relative to its phase at the midpoint of the collision when OD "moves on a P branch" is again given by (5.8). Upon adding $\omega_j t$, we obtain the phase shift of OD for this initial half of the collision, $\alpha - (2\pi R\nu_j/v) + \omega_j t$. Upon subtraction of this quantity for OD from that for OD' we obtain η_r:

$$\eta_r = \gamma - \alpha - (t' + t - R'/v' - R/v)\omega_j . \quad (5.13)$$

The vibrational contribution η_v is again given by

(5.6). One expects that $(t'-R'/v')$ and $t-R/v$ will approximately cancel (e.g., as discussed later) and so $\eta_r+\eta_v$ agrees with the right hand side of (5.13). Similar remarks apply to the phase of the RP' term. These results regarding the RR', PP', PR', and RP' terms also extend as well as to the various terms arising in the $K=2$ case in Table II.

The phase shift terms of both halves of the collision tend to reinforce in a sense in the RR' case, as well as in the PP' one. For example, taking the midpoint of the collision to occur at $t=0$, the difference $t'-R'/v'$ for a "hard sphere" collision is negative and equals, in magnitude, the time required to traverse a distance σ, the hard sphere collision diameter. Similarly, the additional term $-(t-R/v)$, with t and v both negative, equals the same time increment, both in magnitude and in sign, the two terms thus reinforce each other in their sum $t'-t-R'/v'+R/v$. They cancel in the PR' and RP' terms.

The present results may be compared with the nonperturbative classical results of Gordon[11]: His Monte Carlo expression for a transition probability is replaced, in our case, by a semiclassical value given by Eq. (3.16). However, we have a partial probability term, a function of $\bar{w}_l$, rather than a total probability term. His rotational angle between the $\mathbf{j}$ and $\mathbf{j}'$ (our β), and his classical phase shift for the diagonal elements are replaced by our semiclassical ones. He and others have reported that his expression for the line shift is unreliable.[12] Whether ours will remedy this difficulty will be one of the points we will test in a future numerical application of the present paper. The phase shift for the off-diagonal elements in Ref. 11 does not have the cancellation behavior indicated above.

A virtue of semiclassical theory, aside from the fact that it proceeds directly from the quantum mechanical result, is that it can define phase shifts of trajectories in a precise manner (for the diagonal elements $if=i'f'$ at least). For example, in a transition $j\to j'$, the $j'(=j)$ is exactly fixed by singling out certain specific trajectories, while purely classical calculations utilize all possible j''s located within a "box" of $j\pm\frac{1}{2}h$. On the other hand, purely classical calculations have a virtue of considerable simplicity.

Depending on the relative accuracies of the various methods available (exact quantum, classical path, classical, and semiclassical) one may expect to draw upon each of them in future calculations.

Note added in proof. The limits on the semiclassical quantity $J+\frac{1}{2}$ can be shown to be $|l-j|$ and $j+l+1$, and so the limits on J in the integral in Eqs. (3.20), (3.21), (3.26), and (4.4) should read $|l-j|-\frac{1}{2}$ and $l+j+\frac{1}{2}$, instead of $|l-j|$ and $l+j$.

APPENDIX A: SUMMARY OF LIOUVILLE SPACE NOTATION

Liouville space is a Hilbert space whose vectors are operators in the usual Hilbert space $\mathcal{H}$ of bra and ket vectors.[8,20] As such, its vectors are elements of a product space $\mathcal{H}\times\mathcal{H}^\dagger$, $|a\rangle\langle b|$,

$$|a\rangle\langle b| \equiv |a\rangle(|b\rangle)^\dagger \equiv |ab\rangle\rangle\,, \tag{A1}$$

which introduces the notation $|\,\rangle\rangle$ of Baranger.[2b] An element of the dual space is $(|a\rangle\langle b|)^\dagger$, i.e., $|b\rangle\langle a|$, and can be written as

$$|b\rangle\langle a| \equiv (\langle b|)^\dagger\langle a| \equiv \langle\langle ab|\,. \tag{A2}$$

If $|a\rangle\langle b|$ and $|a''\rangle\langle b''|$ are elements, then their usual product, $|a\rangle\langle b|a''\rangle\langle b''|$, is also an element.

The scalar product in this Liouville space can be defined by the customary product space definition,

$$\langle\langle a'b'|ab\rangle\rangle = \langle a'|(\langle b'|)^\dagger|a\rangle(|b\rangle)^\dagger = \langle a'|a\rangle\langle b'|b\rangle^\dagger = \langle a'|a\rangle\langle b|b'\rangle\,, \tag{A3}$$

or by the customary trace of operators, both definitions yielding the same final result:

$$\langle\langle C|D\rangle\rangle = \mathrm{Tr}\,C^\dagger D\,,$$

where C and D denote elements $|a'\rangle\langle b'|$ and $|a\rangle\langle b|$ e.g.,

$$\langle\langle a'b'|ab\rangle\rangle = \mathrm{Tr}(|b'\rangle\langle a'|)(|a\rangle\langle b|) = \langle a'|a\rangle\langle b|b'\rangle\,. \tag{A4}$$

The scalar product $\langle\langle\,|\,\rangle\rangle$, thus defined, has the usual properties of scalar products.

An operator $\hat{A}$ in Liouville space is the direct product of operators in $\mathcal{H}\times\mathcal{H}^\dagger$, e.g., $A_1\times A_2^\dagger$,

$$\hat{A}|ab\rangle\rangle = (A_1|a\rangle)(A_2|b\rangle)^\dagger\,. \tag{A5}$$

The product of $\hat{A}$ with a scalar, and the sum of two $\hat{A}$'s is also an operator in this space. Thus, the Liouville operator $\hat{L}$

$$\hat{L} = [H,I] = H\times I - I\times H \tag{A6}$$

is an operator in this space, I being the identity operator in $\mathcal{H}$ (and in $\mathcal{H}^\dagger$). The product of operators $\hat{A}$ and $\hat{B}$ can also be defined in this space.

From the above rules, the matrix element of the above operator $\hat{A}$ is

$$\langle\langle a'b'|A_1\times A_2^\dagger|ab\rangle\rangle = \langle a'|A_1|a\rangle\langle b|A_2^\dagger|b'\rangle\,. \tag{A7}$$

Frequently, a star notation has been used,[8] instead of the $\times$ notation, so that $A_1\times A_2^\dagger$ is written as $A_1A_2^*$, the star indicating that A_2^* operates on the left hand element,

$$\begin{aligned}\langle\langle a'b'|A_1A_2^*|ab\rangle\rangle &= \mathrm{Tr}\,(A_2^\dagger|b'\rangle\langle a'|)(A_1|a\rangle\langle b|)\\ &= \langle b|A_2^\dagger|b'\rangle\langle a'|A_1|a\rangle\\ &= (A_1)_{a'a}(A_2)^*_{b'b} \equiv \hat{A}_{a'b',ab}\end{aligned} \tag{A8}$$

yielding the same result as in (A7). With this notation $\hat{L}$ would be HI^*-IH^*.

It also follows from the above rules that the matrix element of an operator $\hat{A}$ and a vector ρ, in this space,

$$\hat{A} = A_1 A_2^*, \quad \rho = \sum_{cd} |c\rangle\langle c|\rho|d\rangle\langle d| \equiv \sum_{cd} |c\rangle \rho_{cd} \langle d| , \tag{A9}$$

is

$$\langle\langle a'b'|\hat{A}\rho|ab\rangle\rangle = \sum_{cd} \langle a'|A_1|c\rangle \langle b|A_2^\dagger|b'\rangle \rho_{cd} \langle d|a\rangle . \tag{A10}$$

The Liouville operator L_0^a related to the rotational–vibrational part of the Hamiltonian of the unperturbed absorber, H_0^a is[8,9] $[H_0^a,]$. If we let $|i\rangle$ and $|f\rangle$ be eigenvectors of the Hamiltonian H_0^a in ordinary Hilbert space, with eigenvalues E_i^0 and E_f^0, e.g., if $H_0^a|i\rangle$ equals $E_i^0|i\rangle$, then $|i\rangle\langle f|$, an operator in ordinary Hilbert space, is an eigenvector of L_0^a:

$$L_0^a|if\rangle\rangle = [H_0^a, |i\rangle\langle f|] = \omega_{if}^0 |if\rangle\rangle , \tag{A11}$$

where $\omega_{if}^0 = E_i^0 - E_f^0$. Thus, the eigenvalues of L_0^a in this space are the spectral lines, and the space has been called line space. The matrix elements of L_0^a are seen from (A1) and (A11) to be

$$\langle\langle i'f'|L_0^a|if\rangle\rangle = \omega_{if}^0 \delta_{i'i} \delta_{f'f} . \tag{A12}$$

If $|i\rangle$ and $|f\rangle$ are normalized, it also follows from the above rules that $|if\rangle\rangle$ is also normalized, i.e., that $\langle\langle i'f'|if\rangle\rangle$ equals $\delta_{i'i}\delta_{f'f}$.

The Liouville vector notation in (2.1) and (2.2), where i and f are j_i and j_f, has the following origin[9,20]: With the usual notation for the rotation operator R,

$$R|jm\rangle = \sum_{m'=-j}^{j} D^j_{m'm} |jm'\rangle \tag{A13}$$

the rotation operator $\hat{R}$ in the product space is defined by

$$\hat{R}|j_i m_i, j_f m_f\rangle\rangle = R|j_i m_i\rangle (R|j_f m_f\rangle)^\dagger$$

(i.e., $\hat{R}$ is RR^*), where $|j_i m_i, j_f m_f\rangle\rangle$ is $|j_i m_i\rangle \times \langle j_f m_f|$. One can show that the following Liouville space vector, defined by the right hand side,

$$|\pi_i j_i, j_f \pi_f; \Pi K Q\rangle\rangle = \sum_{m_i m_f} (-1)^{j_i - m_i} \sqrt{2K+1} \times \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} |\pi_i j_i m_i, \pi_f j_f m_f\rangle\rangle \tag{A14}$$

transforms as

$$\hat{R}|j_i j_f; \Pi K Q\rangle\rangle = \sum_{Q'} D^K_{Q'Q} |j_i j_f; \Pi K Q'\rangle\rangle . \tag{A15}$$

In (A14) m_i and m_f are the space-fixed z components of j_i and j_f.

The reduced matrix element is[28]

$$\langle j_i \| X^{\Pi K} \| j_f\rangle = \sum_{m_i m_f} (-1)^{j_i - m_i} (2K+1) \times \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \langle j_i m_i | X_Q^{\Pi K} | j_f m_f\rangle , \tag{A16}$$

where $X^{\Pi K} = \mu$ and $K = 1$, $Q = 0$, $\Pi = -1$ for the z component of the electric dipole operator.

APPENDIX B: RELATION OF FANO'S OPERATOR RESULT TO EQ. (2.4)

The number of translational states in the phase space volume element of $dp_x dp_y dp_z dx dy dz$ is $dp_x dp_y dp_z dx dy dz/h^3$, and hence the number per unit volume is $dp_x dp_y dp_z/h^3$. The number per unit volume with $\mathbf{p}$ in $(\mathbf{p}, \mathbf{p}+d\mathbf{p})$ is thus $p^2 dp d\hat{\mathbf{p}}/h^3$, i.e., $k^2 dk d\hat{k}/(2\pi)^3$, where $d\hat{p}$ and $d\hat{k}$ denote an infinitesimal solid angle, describing the orientation of $\mathbf{p}$ and of $\mathbf{k}$, respectively. Since the number of translational states per unit volume appears in Fano's $N\{m(\omega)\}$, we thus have

$$\sum_{\mathbf{k}} = [1/(2\pi)^3] \int k^2 dk d\hat{k} . \tag{B1}$$

If $|\mathbf{k}\rangle$ denotes the plane wave whose coordinate representative $\langle \mathbf{r}|\mathbf{k}\rangle$ is

$$\langle \mathbf{r}|\mathbf{k}\rangle = \exp i\mathbf{k}\cdot\mathbf{r} , \tag{B2}$$

then $|\mathbf{k}\rangle$ can be decomposed as[29]

$$|\mathbf{k}\rangle \equiv |k\hat{\mathbf{k}}\rangle = \sum_{l,m} |klm\rangle\langle klm|k\hat{\mathbf{k}}\rangle , \tag{B3}$$

where

$$\langle \mathbf{r}|klm\rangle = c_k j_l(kr) Y_{lm}(\hat{\mathbf{r}}) , \tag{B4}$$

$$\langle klm|k\hat{\mathbf{k}}\rangle = (4\pi i^l/c^k) Y_{lm}^*(\hat{\mathbf{k}}) . \tag{B5}$$

j_l and Y_{lm} are the spherical Bessel function and spherical harmonic, respectively. The c_k's are chosen so that the $|klm\rangle$'s have the normalization

$$\langle k'l'm'|klm\rangle = \delta_{ll'}\delta_{mm'}\delta(E-E') . \tag{B6}$$

Using the normalizations of j_l and Y_{lm} one finds (on setting $\hbar = 1$)

$$c_k = (2k\mu/\pi)^{1/2} . \tag{B7}$$

It will be recalled from (2.2) that we shall need

$$\{\mathbf{m}(\omega)\} = \sum_{\mathbf{kk}'} \rho(\mathbf{k}) \langle\langle \mathbf{k}'\mathbf{k}'|\mathbf{m}(\omega)|\mathbf{kk}\rangle\rangle , \tag{B8}$$

where we have used $\mathbf{k} = \zeta$ and where the density operator ρ for the perturber has diagonal elements which depend only on k. The Liouville vectors in (B8) are given with the aid of (B3) by

$$|\mathbf{kk}\rangle\rangle = \sum_{\substack{lm \\ \bar{l}\bar{m}}} |klm, k\bar{l}\bar{m}\rangle\rangle \langle klm|k\hat{\mathbf{k}}\rangle \langle k\hat{\mathbf{k}}|k\bar{l}\bar{m}\rangle . \tag{B9}$$

Further, since

$$\int d\hat{\mathbf{k}} \langle klm | k\hat{\mathbf{k}} \rangle \langle k\hat{\mathbf{k}} | k\bar{l}\bar{m} \rangle = \delta_{l\bar{l}}\, \delta_{m\bar{m}} (2\pi)^3/\mu k \ , \tag{B10}$$

one obtains, on integrating (B8) over $\hat{\mathbf{k}}$ and $\hat{\mathbf{k}}'$,

$$\{\mathbf{m}(\omega)\} = \sum_{\substack{l\,m \\ l'\,m'}} \int_0^\infty \rho(\mathbf{k})\, k^2\, dk \int_0^\infty k'^2\, dk'\, (1/\mu k)\, (1/\mu k') \times \langle\langle k'l'm' | m(\omega) | klm \rangle\rangle \ . \tag{B11}$$

(For later use in (B19) it is helpful to note that in the k' integrand we can write $(k'^2/\mu k')dk'$ as $d(k'^2/2\mu)$.) The Maxwell–Boltzmann distribution function $\rho(\mathbf{k})$ will have the property

$$1 = \sum_{\mathbf{k}} \rho(\mathbf{k}) = [1/(2\pi)^3] \int\int \rho(\mathbf{k})\, k^2\, dk\, d\hat{\mathbf{k}} \ , \tag{B12}$$

and one finds that

$$\rho(\mathbf{k}) = (2\pi/\mu k_B T)^{3/2} \exp(-k^2/2\mu k_B T) \ . \tag{B13}$$

To calculate the matrix elements of $\{m(\omega)\}$ in the uncoupled representation we shall need $\langle\langle j_i' m_i', j_f' m_f' \times | \{m(\omega)\} | j_i m_i, j_f m_f \rangle\rangle$. Thus, in virtue of (B8) and (B9), this calculation involves that of $\langle\langle I'F' | m(\omega) | \times IF \rangle\rangle$, where

$$|I\rangle = |klm j_i m_i\rangle; \ |IF\rangle\rangle = |I\rangle\langle F| = |klm, j_i m_i\rangle\langle klm, j_f m_f| \ , \tag{B14}$$

with $|klm, j_i m_i\rangle$ denoting a vector in the joint perturber–absorber space, $|klm\rangle|j_i m_i\rangle$.

The scalar product $\langle I' | I \rangle$, found from (B6), is

$$\langle I' | I \rangle = \delta(E_{i'} - E_i)\, \delta_{\mathbf{i}'\mathbf{i}} \ , \tag{B15}$$

where E_i is the energy of the absorber–perturber pair in state $|I\rangle$ and where $\delta_{\mathbf{i}'\mathbf{i}}$ now includes $\delta_{m'm}$ and $\delta_{m_i' m_i}$:

$$\delta_{\mathbf{i}'\mathbf{i}} = \delta_{l'l}\, \delta_{m'm}\, \delta_{j_i' j_i}\, \delta_{m_i' m_i} \ . \tag{B16}$$

A matrix element for Fano's expression[8] for the operator $m(\omega)$ is given by[30]

$$\begin{aligned} \langle\langle I'F' | m(\omega) | IF \rangle\rangle \cong {} & \langle I' | T(E_F' + \omega) | I \rangle \langle F | F' \rangle \\ & - \langle I' | I \rangle \langle F' | T(E_I - \omega) | F \rangle^* \\ & + \pi i \delta(E_I' - E_F - \omega) \langle I' | T(E_I') | I \rangle \\ & \times \langle F' | T(E_F) | F \rangle^* \\ & + \pi i \delta(E_F' - E_I + \omega) \langle I' | T(E_I) | I \rangle \\ & \times \langle F' | T(E_F') | F \rangle^* \ , \end{aligned} \tag{B17}$$

where T is the usual scattering theory transition operator.

It is useful to consider the diagonal elements ($if = i'f'$) of (B17) first. We then set $\omega = E_i - E_f = E_i' - E_f'$, since a particular line $i \to f$ is being examined. The first T-matrix element in (B17) is now $\langle I' | T(E_I) | I \rangle$, which may be written as $T_{\mathbf{i}'\mathbf{i}}(E_i)$. Analogous remarks apply to the other elements.

We may then introduce the standard relation[31] for on-the-energy-shell elements

$$S_{\mathbf{i}'\mathbf{i}} = \delta_{\mathbf{i}'\mathbf{i}} - 2\pi i T_{\mathbf{i}'\mathbf{i}} \ . \tag{B18}$$

Upon introducing (B18) into (B17), noting the remark after (B11) that $(k'^2/\mu k')dk'$ equals $d(k'^2/2\mu)$, and using the properties of the δ function we have

$$\int_0^\infty \langle\langle I'F' | m(\omega) | IF \rangle\rangle\, d(k'^2/2\mu) = (2\pi i)^{-1} [\delta_{\mathbf{i}'\mathbf{i}} \delta_{\mathbf{f}'\mathbf{f}} - S_{\mathbf{i}'\mathbf{i}}(E_i) S_{\mathbf{f}'\mathbf{f}}^*(E_f)] \ , \tag{B19}$$

where the k in E_i equals that in E_f. After the manipulations involved in (B21)–(B25), this equation then yields Eq. (2.4) for the diagonal elements.

For the off-diagonal elements the T-matrix elements[7] in (B17) are actually off-the-energy-shell elements. For example, if E_i is written as $E_i^0 + k^2/2\mu$, where E_i^0 is the rotational–vibrational energy of the absorber (emitter), and if E_i' is written as $E_i^{0\prime} + k'^2/2\mu$, an on-the-energy shell element would have $E_i^0 - E_i^{0\prime}$ equal to $(k'^2 - k^2)/2\mu$. Similarly, an on-the-shell requirement would lead to $E_f^0 - E_f^{0\prime}$ also equalling $(k'^2 - k^2)/2\mu$, and thus equalling $E_i^0 - E_i^{0\prime}$, which cannot, in general, be true. However, as Baranger has pointed out previously,[7] such differences can be neglected within the impact approximation.

If, for this off-diagonal case, one subtracts and adds a $\delta_{i'i}/2\pi$ term to each $\langle I' | T | I \rangle$ in the last two terms of (B17), and adds and subtracts a $\delta_{f'f}/2\pi$ to each $\langle F' | T | F \rangle^*$ there, then integrates over $d(k'^2/2\mu)$ using the remark after (B11), one obtains (neglecting differences between E_i' and E_i and between E_f' and E_f),

$$\begin{aligned} \int_0^\infty \langle\langle I'F' | m(\omega) | IF \rangle\rangle\, d(k'^2/2\mu) = {} & \delta_{i'i}\delta_{f'f} \\ & - \tfrac{1}{2}[\delta_{i'i} - 2\pi i \langle I' | T(E_F + \omega) | I \rangle] \\ & \times [\delta_{f'f} - 2\pi i \langle F' | T(E_F) | F \rangle]^* \\ & - \tfrac{1}{2}[\delta_{i'i} - 2\pi i \langle I' | T(E_F' + \omega) | I \rangle] \\ & \times [\delta_{f'f} - 2\pi i \langle F' | T(E_F') | F \rangle]^* \ . \end{aligned} \tag{B20}$$

Noting the remark already made regarding off-the-shell elements, we have written these terms as in (2.4), within the impact approximation.

Equations (B1)–(B20) apply not only to a ($K = 1$, $Q = 0$) case, but to a general KQ case. To obtain a reduced matrix element $\langle\langle i'f'; K'Q' | \{m(\omega)\} | if; KQ \rangle\rangle$, one may use (A14), (B11), (B14), and (B19) to yield

$$\langle\langle i'f'; K'Q' | \{m(\omega)\} | if; KQ \rangle\rangle = -i \int_0^\infty \rho_v 4\pi v^2\, dv \times (v\sigma_{i'f';if}) \ , \tag{B21}$$

where $4\pi\rho_v v^2 dv$ is the normalized Maxwell–Boltz-

mann distribution function of velocities and $\sigma_{i'f';if}$ is a cross section defined by

$$\sigma_{i'f',if}=\frac{\pi}{k^2}\sum_{\substack{ll'mm'\\ m_im_i'm_fm_f'}}\sqrt{(2K+1)(2K'+1)}\,(-)^{-j_i-j_i'-m_i-m_i'}\times\begin{pmatrix}j_i' & j_f' & K'\\ m_i' & -m_f' & -Q'\end{pmatrix}\begin{pmatrix}j_i & j_f & K\\ m_i & -m_f & -Q\end{pmatrix}\times[\delta_{i'i}\delta_{f'f}-S_{i'i}S_{f'f}^{*}]\ , \tag{B22}$$

where $\delta_{i'i}$ is given by (B16). Equation (22) may be transformed to the coupled basis by a standard method briefly mentioned below.

The uncoupled states in the above expression may be related to the coupled states by expressions of the type[32] (omitting n_f and π_f in the bras $\langle\,|$, for brevity)

$$\langle j_fm_flm|=\sum_{J_fM_f}\sqrt{2J_f+1}(-1)^{l-j_f-M_f}\begin{pmatrix}j_f & l & J_f\\ m_f & m & -M_f\end{pmatrix}\times\langle j_flJ_fM_f|\ . \tag{B23}$$

Substitution of expressions like this into (B21), use of the appropriate relationships between the 3-J and 6-J symbols such as[26]

$$\sum_{m_im_fm}(-1)^{j_i+j_f+l+m_i+m_f+m}\begin{pmatrix}j_f & l & J_f\\ m_f & m & -M_f\end{pmatrix}\begin{pmatrix}j_i & l & J_i\\ m_i & m & -M_i\end{pmatrix}\times\begin{pmatrix}j_i & j_f & K\\ m_i & -m_f & -Q\end{pmatrix}=\begin{pmatrix}J_f & J_i & K\\ -M_f & M_i & -Q\end{pmatrix}\begin{Bmatrix}J_f & J_i & K\\ j_i & j_f & l\end{Bmatrix}, \tag{B24}$$

and requiring that angular momentum be conserved in the S-matrices, yields

$$\sigma^{K}_{i'f',if}=\delta_{KK'}\delta_{QQ'}(\pi/k^2)\sum_{ll'J_iJ_f}(-1)^{j_i-j_i'+l-l'}\times(2J_i+1)(2J_f+1)\begin{Bmatrix}J_f & J_i & K\\ j_i & j_f & l\end{Bmatrix}\begin{Bmatrix}J_f & J_i & K\\ j_i' & j_f' & l'\end{Bmatrix}\times[\delta_{i'i}\delta_{f'f}-S^{J_i}_{i'i}S^{J_f*}_{f'f}], \tag{B25}$$

where the subscripts i and f now signify

$$\mathrm{i}\equiv lj_in_i\ ,\qquad \mathrm{f}\equiv lj_fn_f\ . \tag{B26}$$

It will be noted that $\sigma^{K}_{i'f';if}$ is diagonal in K and Q and independent of Q.[9] The diagonal nature of $\{m(\omega)\}$ in (B21) with respect to parity Π arises from the isotropy of the bath of perturbers.[9]

APPENDIX C: PROPERTIES OF THE F_4 GENERATING FUNCTION AND DERIVATION OF EQ. (3.7)

We may let the primed variables in (3.4) be the instantaneous values of the variables along the trajectory, rather than merely the final values. The F_4 is then a generating function for transforming the initial variables to the variables at any point along the trajectory.

There are two F_4 generating functions which we shall consider, both given by Eq. (3.4) and so numerically equal, but one written as $\bar{F}_4(\mathrm{n}'p_R'; \mathrm{n}p_R)$, and the other written as $F_4(\mathrm{n}'E'; \mathrm{n}E)$, where n denotes the totality of quantum numbers. The properties of $\bar{F}_4$ are as follows: The variables canonically conjugate to $2\pi n_i'$, p_R', $2\pi n_i$ and p_R are w_i', R', w_i and R, where n_i and w_i denote the i'th quantum number and angle variable, respectively. The equations for the transformation from unprimed to primed variables follow from (3.4):

$$w_i=\partial\bar{F}_4/\partial(2\pi n_i)\ ,\qquad R=\partial\bar{F}_4/\partial p_R\ ,$$
$$w_i'=-\partial\bar{F}_4/\partial(2\pi n_i')\ ,\qquad R'=-\partial\bar{F}_4/\partial p_R'\ . \tag{C1}$$

These relations are of the standard form for F_4-type generating functions.[23]

When instead the generating function $F_4(\mathrm{n}'E'; \mathrm{n}E)$ is used, the variables canonically conjugate to $2\pi n_i$, E, $2\pi n_i'$, E' are denoted by $\bar{w}_i$, w_E, $\bar{w}_i'$, and w_E', respectively, i.e.,

$$\bar{w}_i=\partial F_4/\partial(2\pi n_i)\ ,\qquad w_E=\partial F_4/\partial E$$
$$\bar{w}_i'=-\partial F_4/\partial(2\pi n_i')\ ,\qquad w_E'=-\partial F_4/\partial E'. \tag{C2}$$

These variables have some striking properties: all the $\bar{w}_i$'s and $\bar{w}_i'$'s are constants of the motion, while w_E and w_E' are "timelike." These results follow when one observes that E serves as the Hamiltonian for the unprimed variables, while E' serves as the Hamiltonian for the primed variables. Thus, using Hamilton's equations of motion, we have

$$\dot{w}_E=(\partial E/\partial E)_{n_i}=1\ ,\qquad \dot{w}_E'=(\partial E'/\partial E')_{n_f'}=1 \tag{C3}$$
$$\bar{w}_i=[\partial E/\partial(2\pi n_i)]_E=0\ ,\qquad \bar{w}_i'=[\partial E'/\partial(2\pi n_i')]_{E'}=0\ . \tag{C4}$$

The relationship of the $\bar{w}$'s and w's is seen as

$$\bar{w}_i=\left(\frac{\partial F_4}{\partial(2\pi n_i)}\right)_E=\left(\frac{\partial\bar{F}_4}{\partial(2\pi n_i)}\right)_{p_R}+\left(\frac{\partial\bar{F}_4}{\partial p_R}\right)_{n_i}\left(\frac{\partial p_R}{\partial(2\pi n_i)}\right)_E=w_i-\frac{R\nu_i}{v}\ ,$$
$$\bar{w}_i'=\left(\frac{\partial F_4}{\partial(2\pi n_i')}\right)_E=\left(\frac{\partial\bar{F}_4}{\partial(2\pi n_i')}\right)_{p_R'}+\left(\frac{\partial\bar{F}_4}{\partial p_R'}\right)_{n_i'}\left(\frac{\partial p_R'}{\partial(2\pi n_i')}\right)_E=w_i'-\frac{R'\nu_i'}{v'}\ , \tag{C5}$$

where in the last step of the equation for $\bar{w}_i'$ we have used the fact that $\bar{w}_i$ is a constant and we have evaluated $\partial p_R'/\partial(2\pi n_i')$ at the end of the trajectory, so that w_i', R', and v' in (3.10) are the postcollision values now, rather than the values at any point during the collision. Related remarks apply to $\bar{w}_i$ in (C5), the last step now being taken at the beginning of the trajectory. The ν_i and ν_i' are the pre- and postcollision values of the ith frequency, $\partial H_0/$

$\partial(2\pi n_i')$, respectively. Since H_0 depends on j and p_R, in Sec. III, but not on J, ν_J is zero, and so we have

$$\bar{w}_J = w_J \ , \quad \bar{w}_J' = w_J \ . \tag{C6}$$

Equations (C2) and (C5) serve to express the partial derivatives in (3.6) in terms of the various angle variables $\bar{w}_j'$, $\bar{w}_j$, w_J', w_J, w_E, and w_E', respectively, which appear in (3.8) and (3.10). Equation (C5) proves (3.10), and there remains now the proof of the last line of (3.8).

Equation (3.4) can be rewritten in terms of the F_2-generating functions from whence it came,[22] by an integration by parts

$$F_4(n'E;\ nE') = F_2(w'R';\ nE) - F_2^0(w'R';\ n'E') \ , \tag{C7}$$

where

$$F_2(w'R';\ nE) = 2\pi \int_w^{w'} n\,dw + \int_R^{R'} p_R\,dR + 2\pi nw + p_R R, \tag{C8}$$

$$F_2^0(w'R';\ n'E') = 2\pi n'w' + p_R'R' \ ,$$

where ndw denotes $\sum n_i\,dw_i$, and similar remarks apply to nw and $n'w'$. We note from (C8) that $2\pi n'$ equals $\partial F_2/\partial w'$ and $\partial F_2^0/\partial w'$, while p_R' equals $\partial F_2/\partial R'$ and $\partial F_2^0/\partial R'$. We recall that w_E equals $\partial F_4/\partial E$ and so equals $\partial F_2/\partial E$, while w_E' similarly equals $-\partial F_4/\partial E'$ and $\partial F_2^0/\partial E'$. Thus, at the point $(w'R')$

$$w_E' = \partial F_2^0/\partial E' = (\partial F_2^0/\partial p_R')(\partial p_R'/\partial E') = R'/v' \quad (v' > 0) \ . \tag{C9}$$

Again, at the point $(w'R')$

$$w_E = \partial F_2/\partial E = w_E(\text{at } wR) + t' - t \ , \tag{C10}$$

where $t' - t$ is the time for the system to go from wR to $w'R'$, recalling that $\dot{w}_E = 1$. However, at the point wR, the two integrals in (C8) vanish and so

$$w_E(\text{at } wR) = \partial F_2/\partial E(\text{at } wR) = R/v \quad (v < 0) \ . \tag{C11}$$

Equations (C9)–(C11) yield the last line of (3.8).

APPENDIX D

Conventionally, if three sucessive Euler angle rotations through the angles α, β, and γ are performed (see Fig. 2), the operation may be described by a rotation operator $D(\alpha\beta\gamma)$. Again, performing two successive sets of three Euler angle rotations in the order α_1, β_1, γ_1 followed by α_2, β_2, γ_2 can be described by a single composite set of three Euler angle rotations α, β and γ. A convenient relationship between the matrix elements of the rotation operators used to describe these rotations is[33]

$$\sum_{m''} D^j_{mm''}(\alpha_2\beta_2\gamma_2)\, D^j_{m''m'}(\alpha_1\beta_1\gamma_1) = D^j_{mm'}(\alpha\beta\gamma) \ , \tag{D1}$$

where[34]

$$D^j_{mm'}(\alpha\beta\gamma) = e^{im'\alpha}\, d^j_{mm'}(\beta)\, e^{im\gamma} = e^{im'\alpha}\, d^j_{m'm}(-\beta)\, e^{im\gamma} \ . \tag{D2}$$

The procedure used here for executing a set of Euler angle rotations is that in Edmonds.[35]

The right hand side of (3.13) can be rewritten by substituting in the relations for θ_1 given by (3.8) and rearranging to give

$$\sum_{\lambda=-K}^{K} e^{i\theta_1} d^K_{\delta\lambda}(\xi)\, d^K_{\delta'\lambda}(\xi') = \sum_{\lambda=-K}^{K} (e^{2\pi i \bar{w}_J' \lambda}\, d^K_{\delta'\lambda}(\xi')\, e^{2\pi i \bar{w}_j' \delta'}) \times (e^{-2\pi i \bar{w}_j \delta}\, d^K_{\lambda\delta}(-\xi)\, e^{-2\pi i w_J \lambda}) \ . \tag{D3}$$

Equations (D1)–(D3) and the right hand side of (3.13) yield

$$\sum_{\lambda=-K}^{K} D^K_{\delta'\lambda}(2\pi w_J',\ \xi',\ 2\pi\bar{w}_j')\, D^K_{\lambda\delta}(-2\pi\bar{w}_j,\ -\xi,\ -2\pi\bar{w}_j) = D^K_{\delta'\delta}(\alpha\beta\gamma) \ , \tag{D4}$$

where the angles α, β, and γ are shown in Fig. 2. This result establishes (3.13).

Equations (D1)–(D3) show that the first set of rotations $(\alpha_1\beta_1\gamma_1)$ in (D1) involves the rotation of $O\bar{D}$ through angles $(-2\pi\bar{w}_j,\ -\xi,\ -2\pi w_J)$, so that $O\bar{D}$ now lies along OY in Fig. 1. The second set of rotations $(\alpha_2\beta_2\gamma_2)$ involves the rotation of this new $O\bar{D}$ into $O\bar{D}'$ via the angles $(2\pi w_J',\ \xi',\ 2\pi\bar{w}_j')$. In Fig. 2 we have used $\bar{q}_j = 2\pi\bar{w}$, $\bar{q}_J = 2\pi w_J$, etc., for clarity in the figure.

*Supported in part by a grant from the National Science Foundation.

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$$\begin{Bmatrix} J_f & J_i & K \\ j_i & j_f & l_i \end{Bmatrix} = \begin{Bmatrix} J_i+m & J_i & K \\ j_i & j_i+\delta & l_i \end{Bmatrix} = \begin{Bmatrix} l_i & j_i & J_i \\ K & J_i+m & j_i+\delta \end{Bmatrix}$$

$$= \frac{(-1)^{l_i+j_i+J_i}}{[\sqrt{(2j_i+1)}\,(2J_i+1)]^{1/2}} d^K_{-m\delta}(\pi-\xi)$$

$$= \frac{(-1)^{l_i+j_i+J_f+K}}{[\sqrt{(2j_i+1)}\,(2J_i+1)]^{1/2}} d^K_{\delta m}(\xi).$$

[19]$I(\omega)$ is the relevant collision-dependent factor appearing in $\mathrm{Im}[\epsilon(0) - \epsilon(\omega)]$ of Eq. (22) in Ref. 9(b). See also Eq. (21) of Ref. 8(a).

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[21]That is, Ref. 15(d), Footnote 8.

[22]That is, see R. A. Marcus, Ref. 15(h), Eq. (2.9), which is the same as the present (3.3).

[23]H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, MA, 1965), p. 242. We have reversed the order of the symbols in F_4. (The primed variables are Goldstein's new variables.)

[24]That is, S. Geltman, *Topics in Atomic Collision Theory* (Academic, New York, 1969), p. 34.

[25]Reference 18, p. 55.

[26]This relation follows from the properties of determinants and was introduced by J. D. Doll and W. H. Miller, J. Chem. Phys. **57,** 5019 (1972) in their "partial averaging" technique.

[27]E. T. Whittaker, *A Treatise on Analytical Dynamics* (Cambridge U.P., Cambridge, 1927), 3rd., p. 339ff; L. A. Pars, *A Treatise on Analytical Dynamics* (Wiley, New York, 1965), p. 573ff.

[28]Reference 18, p. 75.

[29]A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1966), Vol. 1, p. 497, Eq. (B105).

[30]See also Eq. (15) of Ref. 9(b) but note that the first two terms there are in error (they each tacitly contain a product $\delta(E_i' - E_i)\delta(E_f' - E_f)$, instead of one of these δ's above. They should read as in the present Eq. (B17).

[31]Reference 29, Vol. 2, p. 866.

[32]Reference 18, pp. 46, 95.

[33]D. M. Brink and G. R. Satchler, *Angular Momentum* (Clarendon, Oxford, 1968), pp. 146, 147. The rotations carried out in this reference are conventionally different from those in Edmonds. Eq. (D1) applies nevertheless.

[34]Reference 18, pp. 55, 59.

[35]Reference 18, pp. 6, 7.